



Japanese Patent Laid-Open No. 10-233288

Laid-Open Date: September 2, 1998

Application No. 364539/1997

Application Date: December 18, 1997

Convention Priority No. 354937/1996

Convention Priority Date: ~~December 20, 1996~~

Convention Priority Country: Japan (JP)

Applicant: TDK Corporation

Inventors: Michio Arai et al.

[Title of the Invention] ORGANIC EL DEVICE

[Abstract]

[Object] In an organic EL device using a hole injection electrode, particularly a tin- and/or zinc-doped indium oxide transparent electrode, and a layer containing a hole injection transportation compound, particularly a layer containing a tetraarylene diamine derivative, this invention provides an organic EL device capable of improving adhesion between these layers, heat resistance and service life, and preventing a charging phenomenon of charge (electron) after driving and abnormal light emission.

[Construction] An organic EL device includes a layer containing at least 50wt% of a quinolinolate metal complex and having a thickness of not greater than 15 nm between a hole injection

electrode and a layer containing a hole injection transportation compound.

[Claims]

[Claim 1] An organic EL device including a layer containing at least 50wt% of a quinolinolate metal complex and having a thickness of not greater than 15 nm between a hole injection electrode and a layer containing a hole injection transportation compound.

[Claim 2] An organic EL device according to claim 1, wherein a thickness of said layer containing at least 50wt% of said quinolinolate metal complex is not greater than 5 nm.

[Claim 3] An organic EL device according to claim 1 or 2, wherein said hole injection electrode is a transparent electrode.

[Claim 4] An organic EL device according to claim 3, wherein said transparent electrode is a tin- and/or zinc-doped indium oxide electrode.

[Claim 5] An organic EL device according to any of claims 1 through 4, wherein said hole injection transportation compound is a tetraarylene diamine derivative.

[Claim 6] An organic EL device according to any of claims 1 through 5, wherein said layer containing said hole injection transportation compound is a layer having hole injection and/or hole transportation property, and a light emitting layer is

disposed on said layer on the opposite side to said layer containing at least 50wt% of said quinolinolate metal complex.

[Claim 7] An organic EL device according to claim 6, wherein said light emitting layer contains a quinolinolate metal complex.

[Claim 8] An organic EL device according to any of claims 1 through 5, wherein said layer containing said hole injection transportation compound is a mixed layer further containing an electron injection transportation compound, and an electron injection and/or electron transportation layer containing an electron injection transportation compound is disposed on said mixed layer on the opposite side to said layer containing at least 50wt% of said quinolinolate metal complex.

[Claim 9] An organic EL device according to claim 8, wherein said electron injection transportation compound is a quinolinolate metal complex.

[Claim 10] An organic EL device according to any of claims 1 through 9, wherein said quinolinolate metal complex is tris(8-quinolinolate)aluminum.

[Claim 11] An organic EL device according to any of claims 1 through 10, wherein a layer having a hole injection and/or hole transportation property is interposed at least between said light emitting layer and said hole injection electrode, and a layer having electron neutrality and/or electron transportation property is interposed at least between said

light emitting layer and said hole injection electrode.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application]

This invention relates to an organic EL (electroluminescence) device. More particularly, the invention relates to a device that emits light when an electric field is applied to a thin film formed of an organic compound.

[0002]

[Prior Art]

The organic EL device has a construction in which an electron injection electrode and a hole injection electrode sandwich a thin film containing a fluorescent organic compound between them. Electrons and holes are injected to the thin film for recombination to generate exciton. This device utilizes emission of light (fluorescence and phosphorescence) when the exciton is inactivated.

[0003]

It is a feature of the organic EL device that it can generate planar light emission with extremely high luminescence of hundreds to tens of thousands of cd/m² at a voltage of around 10 V, and can emit light of blue to red when suitable kinds of fluorescent materials are selected.

[0004]

A known organic EL device uses a tin-doped indium oxide (ITO) transparent electrode for the hole injection electrode and a tetraarylene diamine derivative for a hole injection transportation compound used for a hole injection transportation layer (Japanese Patent Laid-Open Publication No. 295695/1988).

[0005]

However, this construction involves the problem that when a layer of the tetraarylene diamine derivative such as N,N,N',N'-tetraakis(-m-biphenyl)-1,1'-biphenyl-4,4'-diamine, for example, is directly formed on the ITO transparent electrode, light emission life is not sufficient due to crystallization of the tetraarylene diamine derivative and peel of the layers.

[0006]

To solve such a problem, an attempt has been made to interpose a layer containing 4,4',4"-tris(-N-(-3-methylphenyl)-N-phenylamino)triphenyl-amine (MTDATA) serving also as a hole injection transportation compound between the ITO transparent electrode and the layer containing the tetraarylene diamine derivative so as to acquire the hole injection effect and to improve adhesion between both layers (Japanese Patent Laid-Open Publication No. 308688/1992).

[0007]

However, since this 4,4'4"-tris(-N-

(-3-methylphenyl)-N-phenylamino)triphenylamine has a glass transition temperature of around 80° C, its heat resistance is not sufficient. The organic EL device is used in practice at a high intensity of the electric field and its exothermy is unavoidable. Low heat resistance of this 4,4'4"-tris(-N-(-3-methylphenyl)-N-phenylamino)triphenylamine is critical, and the low heat resistance invites the problem that light emission life is not sufficient.

[0008]

From the structural aspect, the organic EL device exhibits diode characteristics. Therefore, the electron and the hole remain in some cases in the organic layer even when the hole injection electrode is brought to a ground potential after the application of the driving voltage is stopped. When such a charge-up state develops in a matrix driving type display, for example, pixels that are not to be driven emit light during driving of the display and induce an abnormal light emission phenomenon.

[0009]

To prevent such abnormal light emission, another attempt has been made to apply a negative voltage to the hole injection electrode of the organic EL device after the application of the driving voltage is stopped in order to extract the electron and the hole that are charged up.

[0010]

However, it is troublesome to conduct such an operation whenever driving of the organic EL device is stopped. In addition, a circuit for applying the negative voltage is necessary with the result that the circuit construction of the driving circuit and its control become extremely complicated as a whole.

[0011]

[Problems to be Solved by the Invention]

In an organic EL device using a hole injection electrode, particularly a tin- and/or zinc-doped indium oxide transparent electrode, and a layer containing a hole injection transportation compound, particularly a tetraarylene diamine derivative, it is an object of the invention to provide an organic EL device capable of improving adhesion and heat resistance and prolonging service life.

[0012]

It is another object of the invention to provide an organic EL device capable of preventing charging of the charge (electrons) after driving as well as abnormal light emission.

[0013]

[Means for Solving the Problems]

The object described above can be accomplished by the following inventions.

- (1) An organic EL device including a layer containing at least

50wt% of a quinolinolate metal complex and having a thickness of not greater than 15 nm between a hole injection electrode and a layer containing a hole injection transportation compound.

(2) An organic EL device according to (1), wherein a thickness of the layer containing at least 50wt% of the quinolinolate metal complex is not greater than 5 nm.

(3) An organic EL device according to (1) or (2), wherein the hole injection electrode is a transparent electrode.

(4) An organic EL device according to (3), wherein the transparent electrode is a tin- and/or zinc-doped indium oxide electrode.

(5) An organic EL device according to any of (1) to (4), wherein the hole injection transportation compound is a tetraarylene diamine derivative.

(6) An organic EL device according to any of (1) to (5), wherein the layer containing the hole injection transportation compound is a layer having hole injection and/or hole transportation property, and a light emitting layer is disposed on the layer on the opposite side to the layer containing at least 50wt% of the quinolinolate metal complex.

(7) An organic EL device according to (6), wherein the light emitting layer contains a quinolinolate metal complex.

(8) An organic EL device according to (1) to (5), wherein the layer containing the hole injection transportation compound is a mixed layer further containing an electron injection

transportation compound, and an electron injection and/or electron transportation layer containing an electron injection transportation compound is disposed on the mixed layer on the opposite side to the layer containing at least 50wt% of said quinolinolate metal complex.

(9) An organic EL device according to (8), wherein the electron injection transportation compound is a quinolinolate metal complex.

(10) An organic EL device according to any of (1) to (9), wherein the quinolinolate metal complex is tris(8-quinolinolate)aluminum.

(11) An organic EL device according to any of (1) to (10), wherein a layer having a hole injection and/or hole transportation property is interposed at least between the light emitting layer and the hole injection electrode, and a layer having electron neutrality and/or electron transportation property is interposed at least between the light emitting layer and the electron injection electrode.

[0014]

[Embodiment]

An embodiment of the invention will be hereinafter explained in detail. When a layer containing a hole injection transportation compound, preferably such as a tetraarylene diamine derivative, is disposed on a hole injection electrode, preferably such as a tin- and/or zinc-doped indium oxide (ITO,

IZO) transparent electrode, the invention interposes a layer containing at least 50wt% of a quinolinolate metal complex and having a thickness of not greater than 15 nm between them. In consequence, adhesion can be improved between the layer containing the hole injection transportation compound and the hole injection electrode, and light emission life can be prolonged due to the improvement of heat resistance. The electron and the hole charged up in the organic layer can be discharged from the hole injection electrode and abnormal light emission can be prevented. The thickness of the layer containing the quinolinolate metal complex is limited to not greater than 15 nm (150 angstroms) because the quinolinolate metal complex is an electron injection transportation compound, impedes injection of the hole and deteriorates the light emission function of the organic EL device when the thickness exceeds 15 nm. The content of the quinolinolate metal complex must be at least 50wt% because heat resistance cannot be sufficiently improved when the content is less than 50wt%.

[0015]

As described above, the invention stipulates that the content of the quinolinolate metal complex be at least 50wt% and the thickness of the layer be not greater than 15 nm. When these requirements are satisfied, a current flows through the layer containing the quinolinolate metal complex due to the tunnel effect, and the quinolinolate metal complex having high

heat resistance can be used for improving adhesion.

[0016]

Abnormal light emission can be prevented when the layer containing at least 50wt% of the quinolinolate metal complex is disposed on the hole injection electrode. This is presumably because the electron and the hole charged up in the organic layer can be discharged from the hole injection electrode. In other words, the electron and the hole that are charged up can be quickly discharged without applying a negative voltage through a specific circuit when the layer containing the electron injection transportation compound is interposed between the layer containing the hole injection transportation compound and the hole injection electrode.

[0017]

The thickness of the layer containing the quinolinolate metal complex is not greater than 15 nm, preferably from 1 to 12 nm. The content of the quinolinolate metal complex is at least 50wt%, generally from 50 to 100wt%. When the layer contains only the quinolinolate metal complex, its thickness is not greater than 10 nm, preferably from 3 to 7 nm. When the layer contains other compound in combination, particularly when the content of the quinolinolate metal complex is from about 50 to about 90wt%, the thickness of the layer is preferably from 5 to 12 nm.

[0018]

When the layer containing the quinolinolate metal complex is used for particularly suppressing abnormal light emission, its film thickness is not greater than 5 nm, preferably from 2 to 4 nm. This layer may well have a thickness of about 5 nm or below to discharge the electron and the hole that are charged up. When the film thickness is limited to this level, the hole injection transportation function can be further improved. The content of the quinolinolate metal complex is in this case preferably from 70 to 100wt%, more preferably from 70 to 80wt%.

[0019]

The quinolinolate metal complex used in the invention is a quinolinolate metal complex containing 8-quinolinole or its derivative as a legand, particularly preferably its aluminum complex. In this case, the derivative of 8-quinolinole contains a halogen atom or an alkyl group as a substitution group of 8-quinolinole or a benzene ring condensed. Examples of such quinolinolate metal complexes are disclosed in Japanese Patent Laid-Open Publication Nos. 264692/1988, 255190/1991, 70733/1993, 258859/1993, 215874/1994, and so forth.

[0020]

Concrete examples are as follows:

tris(8-quinolinolate)aluminum,
bis(8-quinolinolate)magnesium,
bis(benzo{f}-8-quinolinolate)zinc,

bis(2-methyl-8-quinolinolate)aluminum oxide,
tris(8-quinolinolate)indium,
tris(5-methyl-8-quinolinolate)aluminum,
8-quinolinolate lithium,
tris(5-chloro-8-quinolinolate)gallium,
bis(5-chloro-8-quinolinolate)calcium,
5,7-dichloro-8-quinolinolate aluminum,
tris(5,7-dibromo-8-hydroxyquinolinolate)-
aluminum,
poly[zinc(II)-bis(8-hydroxy-5-quinoliny) methane].

[0021]

Besides 8-quinolinole or its derivative, the quinolinolate metal complex may be those aluminum complexes which have other legands, and concrete examples are as follows:

bis(2-methyl-8-quinolinolate)(phenolate)
aluminum(III),
bis(2-methyl-8-quinolinolate)ortho-cresolate)
aluminum(III),
bis(2-methyl-8-quinolinolate)(metha-cresolate)
aluminum(III),
bis(2-methyl-8-quinolinolate)(para-cresolate)
aluminum(III),
bis(2-methyl-8-quinolinolate)(ortho-phenyl-
phenolate)aluminum(III),
bis(2-methyl-8-quinolinolate)(metha-phenyl-

phenolate)aluminum(III),
bis(2-methyl-8-quinolinolate)(para-phenyl-
phenolate)aluminum(III),
bis(2-methyl-8-quinolinolate)(2,3-dimethyl
phenolate)aluminum(III),
bis(2-methyl-8-quinolinolate)(2,6-dimethyl
phenolate)aluminum(III),
bis(2-methyl-8-quinolinolate)(3,4-dimethyl
phenolate)aluminum(III),
bis(2-methyl-8-quinolinolate)(3,5-dimethyl
phenolate)aluminum(III),
bis(2-methyl-8-quinolinolate)(3,5-di-tert-butyl
phenolate)aluminum(III),
bis(2-methyl-8-quinolinolate)(2,6-diphenylphenolate)alumin
um(III),
bis(2-methyl-8-quinolinolate)(2,4,6-triphenyl
phenolate)aluminum(III),
bis(2-methyl-8-quinolinolate)(2,3,6-trimethyl-
phenolate)aluminum(III),
bis(2-methyl-8-quinolinolate)
(2,3,5,6-tetramethylphenolate)aluminum(III),
bis(2-methyl-8-quinolinolate)(1-naphtholate)
aluminum(III),
bis(2-methyl-8-quinolinolate)(2-naphtholate)
aluminum(III),

bis(2-4-dimethyl-8-quinolinolate)(ortho-phenylphenolate)aluminum(III),
bis(2-4-dimethyl-8-quinolinolate)(para-phenylphenolate)aluminum(III),
bis(2,4-dimethyl-8-quinolinolate)(metha-phenylphenolate)aluminum(III),
bis(2,4-dimethyl-8-quinolinolate)(3,5-dimethylphenolate)aluminum(III),
bis(2,4-dimethyl-8-quinolinolate)(3,5-di-tert-butylphenolate)aluminum(III),
bis(2-methyl-4-ethyl-8-quinolinolate)(para-cresolate)aluminum(III),
bis(2-methyl-4-methoxy-8-quinolinolate)(para-phenylphenolate)aluminum(III),
bis(2-methyl-5-cyano-8-quinolinolate)(ortho-cresolate)aluminum(III), and
bis(2-methyl-6-trifluoromethyl-8-quinolinolate)(2-naphthalate)aluminum(III).

[0022]

The following compounds may also be used:

bis(2-methyl-8-quinolinolate)aluminum(III)- μ -oxo-bis-(2-methyl-8-quinolinolate)aluminum(III),
bis(2,4-dimethyl-8-quinolinolate)
aluminum(III)- μ -oxo-bis-(2,4-dimethyl-8-quinolinolate)

aluminum(III),
bis(4-ethyl-2-methyl-8-quinolinolate)
aluminum(III)- μ -oxo-bis-(4-ethyl-2-methyl-8-
quinolinolate)aluminum(III),
bis(2-methyl-4-methoxyquinolinolate)
aluminum(III)- μ -oxo-bis-(2-methyl-4-methoxy-
quinolinolate)aluminum(III),
bis(5-cyano-2-methyl-8-quinolinolate)
aluminum(III)- μ -oxo-bis-(5-cyanol-2-methyl-8-
quinolinolate)aluminum(III), and
bis(2-methyl-5-trifluoromethyl-8-quinolinolate)
aluminum(III)- μ -oxo-bis-(2-methyl-5-trifluoro-
methyl-8-quinolinolate)aluminum(III).

[0023]

It is particularly preferred to use tris(8-quinolinolate)aluminum in the invention among the metal complexes described above.

[0024]

Only one kind of the quinolinolate metal complex may be used. Alternatively, two or more kinds may be used in combination.

[0025]

The layer containing the quinolinolate metal complex may contain only the quinolinolate metal complex, but other compounds may be used in combination, too. A preferred compound

to be used in combination is a hole injection transportation compound from the aspect of promotion of hole injection. There is no limit in particular to the hole injection transportation compound, and any of the later-appearing compounds may be used.

[0026]

To achieve planar light emission of the organic EL device, at least one of the hole injection electrodes used in the invention must be transparent or translucent. Since the material of the electron injection electrode is limited as will be described later, the material of the hole injection electrode and its thickness are decided so that the transmission factor of emitted light is preferably at least 80%, and the hole injection electrode is preferably a transparent electrode of such an electrode. Concrete preferred examples of the material of the hole injection electrode include tin-doped indium oxide (ITO), zinc-doped indium oxide (IZO), SnO₂ and dopant-doped polypyrrol. The thickness of the hole injection electrode preferably is from about 10 to about 500 nm. To improve reliability of the device, the driving voltage must be low.

[0027]

Preferred are ITO and IZO and their mixture. The oxide composition in these ITO and IZO may somewhat deviate from the stoichiometric composition. In the case of ITO, the composition may be InO₁₋₂ · SnO_{0.8-1.2}. In the case of IZO, the composition may be InO₁₋₂ · Zn_{0.8-1.2}. The proportion of tin oxide in ITO and

the proportion of zinc oxide in IZO are preferably from 12 to 32mol%.

[0028]

The amount of oxygen in ITO may somewhat deviate, though the composition generally contains In_2O_3 and SnO_2 in the stoichiometric composition. The mixing ratio of SnO_2 to In_2O_3 is preferably 1 to 20wt% and further preferably 5 to 12wt%. The mixing ratio of ZnO_2 to In_2O_3 is preferably 12 to 32wt%.

[0029]

The hole injection transportation compound to be contained in the layer disposed on the hole injection electrode having the layer containing the quinolinolate metal complex is preferably a tetraarylene diamine derivative (TPD derivative) expressed by the following formula (1).

[0030]

[Formula 1]

[0031]

In the formula (1) given above, Ary represents an arylene group, n is an integer of 1 to 4, and A_1 to A_4 may be the same or different and represent an aryl group. The arylene group expressed by Ary and the aryl group expressed by A_1 to A_4 may further contain a substitution group such as an alkyl group.

an alkoxy group, an aryl group, an aryloxy group and a halogen atom. A phenylene group is a preferred example of Ary and a phenyl group is a preferred example of A₁ to A₄.

[0032]

Concrete examples of the tetraarylene diamine derivatives are those compounds which are described in Japanese Patent Laid-Open Publication Nos. 295695/1988, 191694/1990, 792/1991, 234681/1993, 239455/1993, 299174/1993, 126225/1995, 126226/1995 and 100172/1996, and EPO650955A1 (corresponding to Japanese Patent Application No. 43564/1995).

[0033]

Among them, the compounds expressed by the following formulas (2) to (5) are preferred examples of the tetraarylene diamine derivatives.

[0034]

[Formula 2]

[0035]

In the formula (2), R₇, R₈, R₉ and R₁₀ respectively represent an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group or a halogen atom, and they may be the same or different. Each of r₇, r₈, r₉ and r₁₀ represents an integer of 0 to 4. R₁₁, R₁₂, R₁₃ and R₁₄ respectively represent an alkyl

group, an alkoxy group, an aryl group, an aryloxy group, an amino group or a halogen atom, and they may be same or different. Each of r_{11} , r_{12} , r_{13} and r_{14} represents an integer of 0 to 5. R_5 and R_6 respectively represent an alkyl group, an alkoxy group, an amino group or a halogen atom, and they may be the same or different. Each of r_5 and r_6 is an integer of 0 to 4.

[0036]

[Formula 3]

[0037]

In the formula (3), R_7 , R_8 , R_9 and R_{10} respectively represent an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group or a halogen atom, and they may be the same or different. Each of r_7 , r_8 , r_9 and r_{10} is an integer of 0 to 4. R_{11} , R_{12} , R_{13} and R_{14} respectively represent an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group or a halogen atom, and they may be the same or different. Each of r_{11} , r_{12} , r_{13} and r_{14} is an integer of 0 to 5. R_5 and R_6 respectively represent an alkyl group, an alkoxy group, an amino group or a halogen atom, and they may be the same or different. Each of r_5 and r_6 is an integer of 0 to 4.

[0038]

[Formula 4]

[0039]

In the formula (4), R₇, R₈, R₉ and R₁₀ respectively represent an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group or a halogen atom, and they may be the same or different. Each of r₇, r₈, r₉ and r₁₀ is an integer of 0 to 4. R₁₁, R₁₂, R₁₃ and R₁₄ respectively represent an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group or a halogen atom, and they may be the same or different. Each of r₁₁, r₁₂, r₁₃ and r₁₄ is an integer of 0 to 5. R₅ and R₆ respectively represent an alkyl group, an alkoxy group, an amino group or a halogen atom, and they may be the same or different. Each of r₅ and r₆ is an integer of 0 to 4.

[0040]

[Formula 5]

[0041]

In the formula (5), Ar₄ and Ar₅ respectively represent a diarylaminoaryl group and they may be the same or different. R₁₅ and R₁₆ respectively represent an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group or a

halogen atom, and they may be the same or different. Each of r_{15} and r_{16} is an integer of 0 to 4. R_7 and R_8 respectively represent an alkyl group, an alkoxy group, an aryloxy group, an amino group or a halogen atom, and they may be the same or different. Each of r_7 and r_8 is an integer of 0 to 5. R_5 and R_6 respectively represent an alkyl group, an alkoxy group, an amino group or a halogen atom, and they may be the same or different. Each of r_5 and r_6 is an integer of 0 to 4.

[0042]

The formulas (2) to (4) will be further explained. In each of these formulas (2) to (4), R_{11} to R_{14} respectively represent an aryl group, an alkyl group, an alkoxy group, an aryloxy group, an amino group or a halogen atom, and they may be the same or different.

[0043]

The aryl group represented by R_{11} to R_{14} may be monocyclic or polycyclic, and includes a condensation ring and a ring group. A total number of carbon atoms is preferably from 6 to 20, and the aryl group may contain a substitution group. Examples of the substitution group in this case are an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group, a halogen atom, and so forth.

[0044]

Concrete examples of the aryl group represented by R_{11} to R_{14} are a phenyl group, an (o-, m-, p-)tolyl group, a pyrenyl

group, a perylenyl group, a coronenyl group, a naphthyl group, an anthrolyl group, a biphenylyl group, a phenylanthrolyl group, a tolylanthrolyl group, and so forth. Particularly preferred among them is the phenyl group. The bonding position of the aryl group, particularly the phenyl group, is preferably the 3-position (meta position to the bonding position of N) or the 4-position (para position to the bonding position of N).

[0045]

The alkyl group represented by R₁₁ to R₁₄ may have a straight chain or a branched chain and preferably has 1 to 10 carbon atoms. They may also have a substitution group. The substitution group in this case is similar to that of the aryl group.

[0046]

Examples of the alkyl group represented by R₁₁ to R₁₄ are a methyl group, an ethyl group, an (n-, i-)propyl group, an (n-, i-, s-, t-)butyl group, and so forth.

[0047]

Examples of the alkoxy group represented by R₁₁ to R₁₄ preferably have 1 to 6 carbon atoms at the alkyl portion and concrete examples are a methoxy group, an ethoxy group, a t-butoxy group, and so forth. The alkoxy group may further be substituted.

[0048]

Examples of the aryloxy group represented by R₁₁ to R₁₄

are a phenoxy group, a 4-methylphenoxy group, 4-(t-butyl)phenoxy group, and so forth.

[0049]

The amino group represented by R₁₁ to R₁₄ may be non-substituted or may have a substitution group, but preferably has a substitution group. Concrete examples are a dimethylamino group, a diethylamino group, a diphenylamino group, a ditolylamino group, a dibiphenylamino group, an N-phenyl-N-tolylamino group, an N-phenyl-N-naphthylamino group, an N-phenyl-N-biphenylamino group, an N-phenyl-N-anthrolylamino group, an N-phenyl-N-pyrenylamino group, a dinaphthylamino group, a dianthrolylamino group, a dipyrenylamino group, and so forth.

[0050]

Examples of the halogen atom represented by R₁₁ to R₁₄ are a chlorine atom and a bromine atom.

[0051]

Symbols r₁₁ to r₁₄ respectively represent an integer of 0 to 5, and are preferably 0 in all of the foregoing formulas (2) to (4).

[0052]

When each of r₁₁ to r₁₄ is an integer of 2 or more, R₁₁ to R₁₄ may be the same or different from one another.

[0053]

In the formulas (2) to (4), examples of the alkyl group,

the alkoxy group amino group and the halogen atom represented by R₅ and R₆ are the same as those mentioned in R₁₁ to R₁₄.

[0054]

Both of r₅ and r₆ are preferably 0. The biphenylene group connecting two arylamino groups is preferably non-substituted.

[0055]

In the formulas (2) to (4), each of R₇ to R₁₀ represents an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group or a halogen atom, and they may be the same or different. Their concrete examples are the same as those of R₁₁ to R₁₄.

[0056]

Each of r₇ to r₁₀ represents an integer of 0 to 4, and is preferably 0.

[0057]

The formula (5) will be further explained. In the formula (5), Ar₄ and Ar₅ respectively represent a diarylaminoaryl group, and they may be the same or different. A diarylaminophenyl group is preferred as the diarylaminoaryl group. Concrete examples are a diphenylaminophenyl group, a bis(biphenyl)aminophenyl group, a biphenylphenylaminophenyl group, a ditolylaminophenyl group, a phenyltolylaminophenyl group, a naphthylphenylaminophenyl group, a dinaphthylaminophenyl group, a phenylpyrenylaminophenyl group, and so forth.

[0058]

In the formulas (5), R_{15} and R_{16} respectively represent an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group or a halogen atom, and they may be the same or different. Their concrete examples are the same as those of R_{11} to R_{14} of the formulas (2) to (4).

[0059]

Symbols r_{15} and r_{16} respectively represent an integer of 0 to 4, and are preferably 0.

[0060]

In the formulas (5), R_{17} and R_{18} respectively represent an alkyl group, an alkoxy group, an aryloxy group, an amino group or a halogen atom, and they may be the same or different. Their concrete examples are the same as those of R_{11} to R_{14} .

[0061]

Each of r_{17} and r_{18} represents an integer of 0 to 5, and is preferably 0.

[0062]

When r_{15} and r_{16} are an integer of 2 or more in the formula (5), a plurality of R_{15} and a plurality of R_{16} may be respectively the same or different. When r_{17} and r_{18} are an integer of 2 or more, a plurality of R_{17} , a plurality of R_{18} and a plurality of R_{19} may be respectively the same or different.

[0063]

In the formula (5), R_5 , R_6 , $r5$ and $r6$ have the same meaning

as defined in the formulas (2) to (4), and r₅ is preferably equal to r₆ (r₅ = r₆ = 0).

[0064]

Concrete examples of the tetraarylenediamine derivatives will be hereinafter illustrated but they do not in any way limit the invention. The concrete examples are expressed by the general formulas (2a) to (5a) and are represented by the combination of R¹, etc, in these formulas. In these examples, H is used when the constituents are all H with the exception of Ar₁ to Ar₆. When the substitution group or groups exist, only the substitution groups are shown with the others being H.

[0065] [Formula 6] to [0085] [Formula 26]

Compound No.

[0086]

The following compounds can also be mentioned as preferred examples.

[0087]

[Formula 27]

[0088]

[Formula 28]

[0089]

These compounds can be synthesized in accordance with the method described in EPO6509551A (corresponding to Japanese Patent Application No. 43564/1995).

[0090]

These compounds have a molecular weight of from about 1,000 to about 2,000, a melting point of from about 200 to about 400° C and a glass transition point of from about 130 to about 200° C. Therefore, they can be obtained as a flat, excellent transparent film under a stable amorphous state even at room temperature or above by ordinary vacuum deposition, and can keep such a condition for a long period. These compounds per se can also be converted to a thin film without using a binder.

[0091]

These tetraarylene diamine derivatives may be used either alone or in combination of two or more kinds.

[0092]

In the invention, the layer containing the tetraarylene diamine derivative that is disposed on the hole injection electrode through the quinolinolate metal complex layer is preferably the hole injection and/or transportation layer, or a light emitting layer as a mixed layer with the electron

injection transportation compound.

[0093]

When the layer containing the tetraarylene diamine derivative is the hole injection and/or transportation layer (that is, the hole injection layer, the hole transportation layer and the hole injection transportation layer), the light emitting layer is preferably disposed on this layer. Furthermore, the electron injection and/or transportation layer (that is, the electron transportation layer, the electron injection layer and the electron injection transportation layer) is disposed on the former. When the light emitting layer uses a phosphorescent material capable of injecting the electron, the light emitting layer functions also as the electron injection and/or transportation layer. Such a construction is preferably used in the invention. The phosphorescent material used for the light emitting layer functioning also as the electron injection and/or transportation layer is the quinolinolate metal complex, among others an aluminum complex, particularly preferably, tris(8-quinolinolate)aluminum.

[0094]

When the layer containing the tetraarylene diamine derivative is used as the light emitting layer of the mixed layer type, the preferred example of the electron injection/transportation compound is the quinolinolate metal complex, among others an aluminum complex, particularly,

tris(8-quinolinolate)aluminum.

The mixing ratio in this case is such that the weight ratio of the hole injection transportation compound to the electron injection transportation compound is generally 10/90 to 90/10, preferably 20/80 to 80/20 and particularly preferably 30/70 to 70/30. It is preferred to further dispose the electron injection and/or transportation layer on this mixed layer. Such a layer uses the quinolinolate metal complex, among others an aluminum complex, particularly preferably, tris(8-quinolinolate)aluminum, as the electron injection transportation compound.

[0095]

In the construction described above, the electron injection electrode is generally disposed on the layer containing the electron injection transportation compound. The electron injection electrode is formed of a material having a small work function, preferably a metal, an alloy or an intermetallic compound having a work function of not greater than 4 eV. Injection efficiency drops when the work function exceeds 4 eV and eventually, light emission efficiency drops, too. Examples of the constituent metals of the electron injection electrode film having a work function of not greater than 4 eV are alkali metals such as Li, Na and K, alkaline earth metals such as Mg, Ca, Sr and Ba, rare earth metals such as La and Ce, and Al, In, Ag, Sn, Zn and Zr. Examples of constituent

alloys of the film having a work function of not greater than 4 eV are Ag · Mg (Ag: 1 to 20at%), Al · Li (Li: 0.5 to 12at%), In · Mg (Mg: 50 to 80at%) and Al · Ca (Ca: 5 to 20at%). They may be used either alone or in combination of two or more kinds, and when they are mixed, a mixing ratio is arbitrary.

[0096]

The crystal grain of the electron injection electrode is preferably small, and is particularly preferably under an amorphous state. The thickness of the electron injection electrode may be a predetermined thickness that insures sufficient injection of the electrons. The thickness is at least 1 nm and preferably 3 nm. Though there is no particular upper limit to the thickness, the film thickness is generally from 3 to 1,000 nm, preferably from 10 to 1,000 nm and particularly preferably from 10 to 500 nm.

[0097]

An auxiliary electrode layer may be disposed on the electron injection electrode layer, that is, on the opposite side to the organic layer. When the film resistance of the electron injection electrode is high or when the film has a thickness having an extent of the minimum electron injection function, the auxiliary electrode lowers the film resistance or supplements insufficiency. When used as a wiring electrode of a simple matrix, the auxiliary electrode prevents the voltage drop and non-uniformity of luminance. When applied to an active

matrix type display using TFT, etc, the auxiliary electrode can speed up the operation.

[0098]

When the auxiliary electrode is allowed to function as a wiring electrode, specific resistance is preferably not greater than 500 $\mu\Omega\cdot\text{cm}$, more preferably not greater than 50 $\mu\Omega\cdot\text{cm}$, particularly preferably not greater than 30 $\mu\Omega\cdot\text{cm}$ and most preferably not greater than 10 $\mu\Omega\cdot\text{cm}$. The lower limit value is 3 to 4 $\mu\Omega\cdot\text{cm}$ as the specific resistance of Al, though this value is not particularly restrictive. Preferred examples of the material of the auxiliary electrode having such a specific resistance are Al, and alloys of Al and transition metals.

[0099]

The auxiliary electrode may well have a predetermined thickness to secure electron injection efficiency and to prevent invasion of moisture, oxygen or an organic solvent. The thickness is preferably at least 50 nm and more preferably at least 100 nm.

[0100]

The material of the substrate is not particularly limited. To take out emitted light from the substrate side, however, the material is a transparent or translucent material such as glass, quartz or resins. A color filter film, a fluorescent substance-containing fluorescence conversion filter film or a dielectric reflection film may be used for the substrate to

control the color of emitted light.

[0101]

It is possible to use a color filter used for liquid crystal displays as the color filter film. In this case, the characteristics of the color filter may be adjusted in match with emitted light from the organic EL to optimize takeout efficiency and color purity.

[0102]

When a color filter capable of cutting off external light of a short wavelength that the EL device material and the fluorescence conversion layer absorb is used, fastness of the device to light and contrast of display can be improved, too.

[0103]

An optical thin film such as a dielectric multi-layered film may be used in place of the color filter.

[0104]

The fluorescence conversion filter film absorbs light of EL emission and causes the phosphor inside the fluorescence conversion film to emit light, thereby effecting color conversion of the color of emitted light. The composition of this film consists of a binder, a fluorescent material and a light absorption material.

[0105]

The fluorescent material may basically be those which have a high fluorescence absorption ratio and preferably exhibit

strong absorption in an EL light emission wavelength region. A laser pigment is practically suitable. It is therefore possible to use Rhodamine compounds, perillene compounds, cyanine type compounds, phthalocyanine type compounds (including sub-phthalocyanine type), naphthaloimide type compounds, condensed ring hydrocarbon compounds, condensed heterocyclic compounds, styryl type compounds and coumarin type compounds.

[0106]

The binder is basically selected from those materials which do not extinct fluorescence, and are preferably capable of fine patterning such as photolithography and printing. Preferably, these materials are not damaged during the formation of the ITO film.

[0107]

The light absorption material is used when light absorption of the fluorescent material is not sufficient. Therefore, it may not be used unless necessary. The light absorption material may be selected from those which do not extinct fluorescence of the fluorescent material.

[0108]

The foregoing explanation has mainly been given on the construction of the laminate type of the construction of the organic compound interposed between the hole injection electrode having the layer containing the quinolinolate metal

complex and the electron injection electrode. In other words, the hole injection and/or transportation layer containing the tetraarylene diamine derivative is disposed from the hole injection electrode side, and the light emitting layer containing the quinolinolate metal complex is further disposed. The explanation has also dealt with the construction of the light emitting layer of the mixed layer type of the tetraarylene diamine derivative and the quinolinolate metal complex. However, the invention is not limited to such a construction, and other constructions are arbitrary so long as the layer containing the quinolinolate metal complex is interposed between the hole injection electrode and preferably the layer containing the hole injection transportation compound such as the tetraarylene diamine derivative.

[0109]

The organic compounds other than those described above, that can be contained in the organic compound layer in other constructions, or the organic compounds that can be used in combination with the organic compound layer having the preferred construction described above, are as follows.

[0110]

The fluorescent material that can be used for the light emitting layer in the invention is at least one kind of the compounds described in Japanese Patent Laid-Open Publication No. 264692/1988 such as quinacridone, rubrene and styryl

pigments, coumarin and their derivatives. Also, tetraphenylbutadiene, anthracene, perylene, coronene and 12-phthaloperynone derivatives can be used. Further, it is possible to use phenylanthracene derivatives described in Japanese Patent Laid-Open Publication No. 12600/1996 and the tetraanyl ethene derivative described in Japanese Patent Laid-Open Publication No. 12969/1996.

[0111]

The hole injection transportation compounds for the hole injection and/or transportation layer can use various organic compounds described in Japanese Patent Laid-Open Publication Nos. 295695/1988, 191694/1990 and 792/1991. Examples are aromatic tertiary amines other than the tetraarylene diamine derivatives of the formula (1), hydrazone derivatives, carbazole derivatives, triazole derivatives, imidazole derivatives, oxadiazole derivatives having an amino group and polythiophene derivatives.

[0112]

The electron injection and/or transportation layer can use oxadiazole derivatives, perylene derivatives, pyridine derivatives, pyrimidine derivatives, quinoxaline derivatives, diphenylquinone derivatives, nitro-substituted fluorene derivatives, and so forth.

[0113]

The thickness of each of the light emitting layer, the

hole injection transportation layer and the electron injection transportation layer is not particularly limited but varies depending on the formation method. The thickness is generally from 5 to 1,000 nm, preferably from 5 to 500 nm, more preferably from 10 to 300 nm and most preferably from 10 to 200 nm.

[0114]

The thickness of each of the hole injection transportation layer and the electron injection transportation layer may be equal to, or from 1/10 to 10 times the thickness of the light emitting layer, though it varies depending on the design of the rebinding/light emitting region. When the electron or hole injection layer is separated from the electron or injection transportation layer, the thickness of the injection layer is at least 1 nm while the thickness of the transportation layer is at least 1 nm, particularly at least 20 nm. The upper limit of the thickness of these injection and transportation layers is generally about 500 nm, more preferably about 100 nm for the injection layer and is about 1,000 nm, more particularly about 500 nm for the transportation layer. This film thickness also holds true of the case where two injection transportation layers are disposed.

[0115]

The thickness of the mixed layer is from a thickness corresponding to that of one molecular layer to less than the film thickness of the organic compound layer. More concretely,

it is preferably from 1 to 85 nm, more preferably from 5 to 60 nm and most preferably from 5 to 50 nm.

[0116]

In the invention, it is preferred to employ a gaseous phase growing method such as vacuum deposition and sputtering to form the electron injection electrode and the hole injection electrode.

[0117]

Though the electron injection electrode and the hole injection electrode can be formed through vacuum deposition, it is preferred to employ sputtering, more preferably DC sputtering, and particularly preferably pulse sputtering. Power of DC sputtering is preferably within the range of 0.1 to 10 W/cm², particularly preferably from 0.5 to 7 W/cm². The film formation rate is preferably from 0.1 to 100 nm/min, particularly preferably from 1 to 30 nm/min.

[0118]

The sputtering gas is not particularly limited. It is preferred to use an inert gas such as Ar, He, Ne, Kr and Xe, or their mixed gas. The pressure at the time of sputtering by such a gas is generally from 0.1 to 20 Pa.

[0119]

To form the layer containing quinolinolate metal complex, the hole injection and/or transportation layer, the light emitting layer and the electron injection and/or transportation

layer over the hole injection electrode, vacuum deposition is preferably employed because it can form uniform thin films. When vacuum deposition is employed, it provides uniform thin films under the amorphous state or the films having a crystal grain size of not greater than 0.1 μm . (Generally, the lower limit value is about 0.001 μm). When the crystal grain size exceeds 0.1 μm , light emission becomes non-uniform. In consequence, the driving voltage of the device must be increased and injection efficiency of the charge remarkably drops.

[0120]

The vacuum deposition condition is not limited, in particular. The vacuum is not higher than 10^{-3} Pa (10^{-5} Torr), more preferably 10^{-4} Pa. The deposition rate is preferably from about 0.1 to 1 nm/sec. Each layer is preferably formed continuously in vacuum. When the films are continuously formed in vacuum, it becomes possible to prevent adsorption of impurities to the interfaces among the layers and hence, to obtain high performance. Furthermore, the driving voltage of the device can be lowered.

[0121]

When one layer contains a plurality of compounds during the formation of these layers by vacuum deposition, it is preferred to discretely control the temperature of each port storing therein the compound and to conduct co-deposition. However, the compounds may be mixed in advance and may be then

vacuum deposited. Besides vacuum deposition, it is also possible to employ solution coating methods (spin coating, dipping, casting, etc) and a Langmuir-Blodgett method (LB). When the solution coating method is employed, each compound may be dispersed in a matrix material such as a polymer.

[0122]

In connection with this point, the method of forming the mixed layer in the invention is preferably co-deposition that conducts vacuum deposition from different vacuum deposition sources. However, when the deposition pressures (deposition temperatures) are substantially or extremely equal to one another, it is possible to conduct vacuum deposition by mixing in advance the materials inside the vacuum port. The compounds are preferably mixed uniformly in the mixed layer, but may exist in the island form in some cases.

[0123]

The organic EL device according to the invention is generally used as a DC driving type EL device, but it can be driven by AC driving or pulse driving. An impressed voltage is generally from about 2 to about 20 V.

[0124]

[Examples]

The invention will be explained in further detail with reference to examples thereof.

[Example 1]

A glass substrate having a 100 nm-thick ITO transparent electrode (hole injection electrode) was subjected to ultrasonic washing with a neutral detergent, acetone and ethanol. After the substrate was pulled out from boiling ethanol and dried, it was washed with UV ozone. The substrate was then fixed to a substrate holder of a vacuum deposition apparatus and the pressure was reduced down to 1×10^{-6} Torr. Incidentally, ITO had a composition of In_2O_3 (90mol%) - SnO_2 (10mol%).

[0125]

Next, tris(8-quinolinolate)aluminum (Alq_3) was vacuum deposited to a thickness of 5 nm at a vacuum deposition rate of 0.2 nm/sec.

[0126]

Further, $\text{N},\text{N},\text{N}',\text{N}'\text{-tetraakis}(-\text{m-biphenyl})-1,1'$ -biphenyl-4,4'-diamine (Compound No. 2-1) was vacuum deposited to a thickness of 80 nm at a deposition rate of 2 nm/sec to form a hole injection transportation layer.

[0127]

Next, tris(8-quinolinolate)aluminum was vacuum deposited to a thickness of 30 nm at a deposition rate of 1 nm/sec to form a light emitting layer (functioning also as an electron injection transportation layer).

[0128]

While the vacuum condition was kept, MgAg (weight ratio of 10:1) was vacuum deposited to a thickness of 200 nm at a

deposition rate of 0.2 nm/sec. The resulting EL device was called "Sample No. 1".

[0129]

Sample No. 2 was obtained in the same way as in Sample No. 1 with the exception that the tris(8-quinolinolate)aluminum layer was not formed on the hole injection electrode.

[0130]

Sample No. 3 was obtained in the same way as in Sample No. 1 with the exception that the thickness of the tris(8-quinolinolate)aluminum layer formed on the hole injection electrode was changed to 20 nm.

[0131]

Further, Sample No. 4 was obtained in the same way as in Sample No. 1 with the exception that a layer of 4,4',4"-tris(-N-(3-methylphenyl)-N-phenylamino)triphenylamine (MTDATA) was formed to a thickness of 40 nm on the hole injection electrode in place of tris(8-quinolinolate)aluminum.

[0132]

Sample No. 5 was obtained in the same way as in Sample No. 1 with the exception that tris(8-quinolinolate)aluminum and 4,4',4"-tris(-N-(3-methylphenyl)-N-phenylamino)triphenylamine (MTDATA) were vacuum co-deposited to a weight ratio of 60:40 and to a thickness of 10 nm on the hole injection electrode.

[0133]

A voltage was impressed on Samples Nos. 1 to 5 under a condition of 7.5 V 10 mA/cm², and half-life of luminance at initial luminance of 300 cd/m² was determined at 60° C in a N₂ atmosphere. Table 1 shows the result.

[0134]

[Table 1]

Sample No.	layers on anode compound	Thickness (nm)	life (hour)
1	Alq3	5	2,000
2	-	-	500
3	Alq3	20	(no light emission)
4	MTDATA	40	350
5	Alq3(60)+MTDATA(40)	10	1,500

[0135]

It can be clearly seen from Table 1 that heat resistance could be improved and light emission life could be prolonged when the layer containing tris(8-quinolinolate)aluminum and having a thickness of 15 nm or below was disposed on the hole injection electrode.

[00136]

[Example 2]

In this example, N,N,N',N'-tetraakis(-m-biphenyl)-1,1'-biphenyl-4,4'-diamine and tris(8-quinolinolate)aluminum were vacuum co-deposited in such a fashion as to attain a weight ratio of 50:50 and to form a mixed layer type light emitting layer having a thickness of

50 nm in place of the laminate structure of the hole injection transportation layer of N,N,N',N'-tetraakis(-m-biphenyl)-1,1'-biphenyl-4,4'- diamine and the light emitting layer of tris(8-quinolinolate)aluminum in Samples Nos. 1 to 5 of Example 1. Further, an electron injection transportation layer of tris(8-quinolinolate)aluminum was vacuum deposited to a thickness of 30 nm on this light emitting layer, and an electron injection electrode was formed on the former to give organic EL devices. These samples were called "Samples Nos. 21 to 25" corresponding to Samples Nos. 1 to 5 of Example 1.

[0137]

Characteristics of these samples Nos. 21 to 25 were examined in the same way as in Example 1. Table 2 represents the result.

[0138]

[Table 2]

Sample No.	layers on anode compound	Thickness (nm)	life (hour)
21	Alq3	5	3000
22	-	-	850
23	Alq3	20	no light emission
24	MTDATA	40	800
25	Alq3(60)+MTDATA(40)	10	2500

[0139]

It can be clearly seen from Table 2 that heat resistance could be improved and light emission life could be prolonged when the layer containing tris(8-quinolinolate)aluminum and

having a thickness of 15 nm or below was disposed on the hole injection electrode.

[0140]

[Example 3]

Samples Nos. 31 to 44 of organic EL devices were obtained in the same way as in Samples Nos. 1 and 5 of Example 1 with the exception that the compounds Nos. 5-2, 5-3, 5-10, 5-12, 6-1, 6-2 and 6-3 tabulated already were used in place of N,N,N',N'-tetraquais(-m-biphenyl)- 1,1'-biphenyl-4,4'-diamine as the material for the hole injection transportation layer. Characteristics of these samples were examined in the same way as in Example 1. It was confirmed that these samples exhibited the excellent result equivalent to that of Samples Nos. 1 and 5 of Example 1 depending on their constructions.

[0141]

[Example 4]

Samples Nos. 51 to 64 of the organic EL devices were obtained in the same way as in Samples Nos. 21 and 25 of Example 2 with the exception that the compounds Nos. 5-2, 5-3, 5-10, 5-12, 6-1, 6-2 and 6-3 tabulated already were used in place of

N,N,N',N'-tetraquais(-m-biphenyl)-1,1'-biphenyl-4,4'-diamine as the material for the light emitting layer of the mixed layer type. Characteristics of these samples were examined

in the same way as in Example 1. It was confirmed that these samples exhibited the excellent result equivalent to that of Samples No. 21 of Example 2 depending on their constructions.

[0142]

[Example 5]

In the samples of Examples 1 to 4 of the invention, IZO was used for the transparent electrode in place of ITO. An excellent result equivalent to that of the samples of Examples 1 to 4 of the invention could be obtained.

[0143]

Incidentally, IZO had a composition of In_2O_3 (95mol%) - SnO_2 (5mol%).

[0144]

[Example 6]

In Sample No. 1 of example 1, the ITO transparent electrode was formed to a predetermined pattern, and the organic layers such as the light emitting layer were formed in the same way as in Sample No. 1 of Example 1. Next, the electron injection electrode of Example 1 was formed to a predetermined pattern, and a glass seal plate was disposed on the former to produce an organic EL display having pixels of $300 \times 300 \mu\text{m}$ and 256 x 64 dots.

[0145]

The resulting organic EL display was matrix driven so as to attain the same light emitting condition as that of Example

1, and the condition of each pixel was observed with eye. In the driving circuit used at this time, the hole injection electrode was connected to the driving power source side during driving and was connected to the ground side (ground potential) during non-driving.

[0146]

As a result, no abnormal light emission was confirmed when the display was driven at a 1/64 duty for 1,000 hours.

[0147]

[Effect of the Invention]

Since the invention uses the quinolinolate metal complex excellent in heat resistance, the invention can improve adhesion between the hole injection electrode and the layer containing the hole injection transportation layer and can prolong light emission life.

[0148]

The invention can also prevent the charge phenomenon of the charge (electron) after driving and eventually, abnormal light emission.